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ORIGINAL ARTICLE

Removal of toxic metals with activated carbon prepared from *Salvadora persica*

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Abstract Activated carbon was prepared under vacuum from *Salvadora persica*. Three different activated carbon samples were prepared for 30, 45 and 60 min duration at 400 °C. The surface area, pore volume and pore diameter of the activated carbon decrease with increase in the heating time. Activated carbon was used for sorption of copper, lead and nickel from aqueous solutions. The Langmuir sorption isotherm indicated maximum sorption capacities for the copper. The maximum sorption capacity was also found for the activated carbon which was heated for 30 min. The experimental data were applied to the Langmuir, the Freundlich and the Temkin sorption isotherms using both linear and non linear regression methods. The Langmuir model type 1 provided the lowest error values and fit better to experimental data compared with the other two models.

1. Introduction

Environmental pollution through industrial effluents has been a serious concern in developing countries. To protect our environment from pollutants, it can be achieved either by minimizing the introduction of pollutants into the environment or by their removal from contaminated media (Baker and Khalili, 2004). Heavy metals have been excessively added to the environment due to rapid industrialization. As a result these toxic metals from industrial effluents have often been detected on river banks. The toxic metals originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries. These heavy metals are not biodegradable as a consequence their presence in water causes serious health problems in human, plants and animals. Wastewater commonly contains copper, nickel and lead (Xie et al., 1996; Ngah and Fatinathan, 2008). Excessive intake of copper can cause capillary damage, hepatic toxicity, and renal damage (Ajmal et al., 1998). Exposure to nickel results in skin irritation, damage to lungs, and mucous membrane (Oliver, 1997). The presence of lead in drinking water causes various health disorders and causes enzyme inhibition. Importantly, the inorganic form of lead is reported to exert drastic effects as compared with organic isoforms (Volesky, 1990; Lo et al., 1999). Some heavy metals cause cancer; therefore it is necessary to remove toxic heavy metal ions from wastewater in order to protect human and

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environmental health. Much attention has been paid to the removal of toxic heavy metal ions from industrial effluents in recent years (Zdemir et al., 2005; Meunier et al., 2006). The removal of heavy metals from the environment can be divided into biotic and aboitic methods. Boitic methods mean the removal of heavy metals by plants or microorganisms while aboitic methods consist of physiochemical processes such as precipitation, co-precipitation, electrochemical treatment, ion exchange, liquid–liquid extraction, resins, cementation, electrodialysis and sorption (Lothenbach et al., 1997; Ng et al., 2002; Qin et al., 2007). Among these methods, sorption is one of the most effective, economic and simplest methods for the removal of pollutants from wastewaters (Huang and Hao, 1989). Among the different sorbents that have been conventionally used for the removal of heavy metals from solution are zeolite (Zamzow et al., 1990), clay (Sikalidis et al., 1989), and activated charcoal (Faust and Ali, 1983). Activated carbon is widely applied as sorbent due to its high sorption capacity, the sorption capacity is related to the surface characteristics (surface area, pore size and pore volume) of the activated carbon, while surface characteristics of the activated carbon depend on preparation conditions (Hassler, 1993; Mattson and Mark, 1971; Hassler, 1974).

The purpose of the present study is to prepare activated carbon from the medicinal plant (*Salvadora persica*) under vacuum at different soaking times. The physical parameters such as surface area, pore volume and pore diameter will be determined. The activated carbon will be used to remove copper, lead and nickel from aqueous solution by sorption method. The three most commonly used equilibrium models (Langmuir, Freundlich and Temkin) will be applied to sorption studies. Both linear and nonlinear regression techniques will be used for the sorption process. Four different linear forms of Langmuir models will be applied to sorption studies to have better comparison between linear and nonlinear regression techniques.

2. Experimental

2.1. Materials

S. persica root were obtained from the local market in Peshawar, Khyber Pakhtunkhwa, Pakistan. Ortho-phosphoric acid 85% purity (Merck) was used as activation agent. Hydrochloric acid (Merck), sodium hydroxide (Merck), lead (Merck), nickel (Merck) and copper (Merck) nitrates (analytical grade) were used.

2.2. Characterization

The surface area and pore size of the sorbent were determined by BJH-N_2 adsorption method using Surface Area Analyzer Automatic Quantachrome Nova Win 2 2200e-UK and a Quantachrome Autosorb, using nitrogen gas at 77 K. The samples were degassed for 13 h at 373 K in vacuum prior to the nitrogen adsorption measurements at 77 K. Gallen Hamp (England) tube furnace was used for the preparation of activated carbon. The amount of cation sorbed was determined using a Perkin Elmer 700 AAS apparatus, keeping in mind the difference between the initial concentration in the aqueous solution and that found in the supernatant after the sorption process. The reproducibility was checked at least through one duplicate run for each experimental point.

2.3. Preparation of activated carbon

S. persica roots were acquired from a local store at Peshawar, Pakistan. The roots were cleaned and washed thoroughly. The cleaned roots were dried in an oven at 105 °C for 4 h. Then powdered with a grinder and kept in a desiccator as raw material for activated carbon preparation.

For impregnation purposes, 20 g of the powdered sample was added to 200 cm^3 of 10% (v/v) ortho-phosphoric acid solution and impregnated for 14 h. The calculated impregnation ratio was 1:1.4 (Molina-Sabio and Rodrigues-Reinoso, 2004). After impregnation, the sample was washed several times with distilled water up to neutral pH. After washing, the sample was dried in an oven for 8 h at 105 °C. The dried sample was then carbonized in a tube furnace under vacuum at 400 °C at 30 min, 45 min, and 60 min, respectively. The activated carbon was cooled to room temperature under vacuum and transferred to desiccators for further use.

2.4. Sorption experiments

Sorption experiments were carried out by adding nearly 20 mg of the activated carbon into a series of polyethylene flasks containing 20.0 cm^3 of metallic cation solution having concentrations ranging from 4.0×10^{-4} to 8.0×10^{-3} mol dm^{-3} to evaluate the sorption capacity. All experiments were performed in duplicate in a batch wise process in an orbital bath at 298 ± 1 K. In order to obtain the time needed to reach isotherm saturation, kinetic experiments were assayed using similar cation solutions at pH 4 for copper and nickel and pH 3 for lead. For this determination, the amount of cation removal as a function of time defined a plateau at 4 h. However, the chosen time was 5 h to ensure the best equilibrium conditions. The supernatant solutions were separated from the solid through decantation and aliquots of supernatant were taken to determine the amounts of cation remaining through atomic absorption spectrophotometer. The amount of the cation sorbed onto activated carbon was calculated by Eq. (1),

$$Nf = \frac{ni - ns}{m} \quad (1)$$

where Nf is the number of moles sorbed on activated carbon (mmol g^{-1}), ni and ns are the number of moles in the initial solution and the supernatant after equilibrium and m is the mass of the sorbent used in each sorption process (Khan et al., 2011).

Table 1 Porosity of activated carbon as determined by nitrogen adsorption.

Time (min)	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (Å)
30	375	1.21	128.97
45	221.54	0.67	123.5
60	27.07	0.03	35.32

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Table 2 Number of moles sorbed (*Nf*), Langmuir parameters (N_s and *b*), coefficient of determination (R^2) and standard error (SE) for the interaction of divalent metals with activated carbon (prepared at 400 °C for 30, 45, and 60 min) at 25 °C, using different linear form of the Langmuir isotherm.

Time (min)	Isotherm	Parameter	Type I	Type II	Type III	Type IV
30	Cu(II)	*Nf* (mmol g^{-1})	1.17	1.17	1.17	1.17
		N_s (mmol g^{-1})	1.22 ± 0.21	1.31 ± 0.26	1.30 ± 1.30	1.31 ± 3.52
		b (g $mmol^{-1}$)	3.71 ± 0.81	2.69 ± 0.28	2.76 ± 0.36	2.67 ± 2.67
		R^2	0.996	0.996	0.964	0.964
		SE	0.03	0.053	0.052	0.061
		χ^2	0.009	0.017	0.017	0.018
	Pb(II)	*Nf* (mmol g^{-1})	1.01	1.01	1.01	1.01
		N_s (mmol g^{-1})	1.13 ± 0.50	1.43 ± 0.69	1.24 ± 1.24	1.35 ± 1.39
		b (g $mmol^{-1}$)	1.73 ± 0.88	0.92 ± 0.75	1.25 ± 0.79	1.03 ± 1.03
		R^2	0.989	0.973	0.798	0.798
		SE	0.06	0.11	0.070	0.093
		χ^2	0.037	0.10	0.047	0.081
	Ni(II)	*Nf* (mmol g^{-1})	0.93	0.93	0.93	0.93
		N_s (mmol g^{-1})	1.01 ± 0.61	1.05 ± 0.94	1.05 ± 1.05	1.06 ± 1.44
		b (g $tmol^{-1}$)	1.60 ± 0.98	1.39 ± 0.68	1.38 ± 0.72	1.35 ± 1.35
		R^2	0.997	0.991	0.972	0.972
		SE	0.018	0.025	0.025	0.025
		χ^2	0.001	0.008	0.008	0.008
	Cu(II)	*Nf* (mmol g^{-1})	0.94	0.94	0.94	0.94
		N_s (mmol g^{-1})	1.08 ± 0.58	1.29 ± 0.07	1.17 ± 0.09	1.30 ± 1.22
		b (g $mmol^{-1}$)	1.58 ± 0.91	0.94 ± 0.07	1.24 ± 0.17	0.94 ± 0.94
		R^2	0.983	0.930	0.721	0.721
		SE	0.055	0.08	0.65	0.81
		χ^2	0.048	0.05	0.075	0.050
45	Pb(II)	*Nf* (mmol g^{-1})	0.80	0.80	0.80	0.80
		N_s (mmol g^{-1})	0.96 ± 0.89	1.05 ± 0.03	1.02 ± 0.03	1.04 ± 0.05
		b (g $mmol^{-1}$)	1.15 ± 1.03	0.90 ± 0.04	0.98 ± 0.09	0.92 ± 0.08
		R^2	0.991	0.986	0.933	0.933
		SE	0.019	0.021	0.026	0.026
		χ^2	0.001	0.007	0.008	0.008
	Ni(II)	*Nf* (mmol g^{-1})	0.83	0.83	0.83	0.83
		N_s (mmol g^{-1})	0.90 ± 0.08	0.97 ± 0.02	0.95 ± 0.02	0.96 ± 0.06
		b (g $mmol^{-1}$)	1.91 ± 0.01	1.36 ± 0.01	1.46 ± 0.04	1.41 ± 0.09
		R^2	0.997	0.996	0.964	0.964
		SE	0.035	0.027	0.031	0.033
		χ^2	0.009	0.010	0.012	0.015
60	Cu(II)	*Nf* (mmol g^{-1})	0.83	0.83	0.83	0.83
		N_s (mmol g^{-1})	0.87 ± 0.06	0.93 ± 0.02	0.93 ± 0.93	1.31 ± 2.51
		b (g $mmol^{-1}$)	3.71 ± 0.02	2.69 ± 0.007	2.76 ± 0.36	2.67 ± 2.67
		R^2	0.996	0.996	0.964	0.964
		SE	0.027	0.033	0.035	0.30
		χ^2	0.08	0.011	0.012	0.13
	Pb(II)	*Nf* (mmol g^{-1})	0.64	0.64	0.64	0.64
		N_s (mmol g^{-1})	0.69 ± 0.13	0.85 ± 0.13	0.56 ± 0.12	0.84 ± 0.14
		b (g $mmol^{-1}$)	2.25 ± 0.04	1.15 ± 0.11	1.75 ± 0.12	1.20 ± 0.27
		R^2	0.990	0.881	0.647	0.647
		SE	0.05	0.069	0.055	0.06
		χ^2	0.03	0.058	0.042	0.05
	Ni(II)	*Nf* (mmol g^{-1})	0.55	0.55	0.55	0.55
		N_s (mmol g^{-1})	0.58 ± 0.07	0.64 ± 0.12	0.61 ± 0.03	0.64 ± 0.33
		b (g $mmol^{-1}$)	5.04 ± 0.03	3.17 ± 0.07	3.87 ± 0.05	3.09 ± 0.69
		R^2	0.997	0.866	0.756	0.756
		SE	0.031	0.034	0.033	0.034
		χ^2	0.010	0.014	0.011	0.014

2.5. Isotherm models

Equilibrium isotherm equations are used to portray the experimental sorption process. The equation parameters and the equilibrium models provide information about the sorption mechanisms, the surface properties and affinities of the sorbent. The three most common isotherms for describing sorption systems are the Langmuir, the Freundlich and the Temkin isotherms.

2.5.1. Langmuir isotherm model

The Langmuir isotherm theory assumes the monolayer coverage of sorbate over a homogenous sorbent surface. Therefore, at equilibrium, a saturation point is reached where no further sorption can occur. It means that the sorption takes place at the specific homogeneous sites within the sorbent. Once a cation occupies a site, no further sorption can use the same place (Oh et al., 2009). The mathematical expression of the modified Langmuir isotherm model is expressed in Eq. (2),

$$\frac{C_m}{Nf} = \frac{C_s}{N_s} + \frac{1}{\mathrm{Nsb}} \tag{2}$$

where Nf is the sorption capacity at equilibrium, C_s is the equilibrium concentration, N_s and b are the Langmuir constants related to the maximum sorption capacity and the sorption energy, respectively. Maximum sorption capacity Ns represents the monolayer coverage of sorbent species with sorbate and b represents the energy of sorption (Badshah and Airoldi, 2011; Allen et al., 2004).

2.5.2. Freundlich isotherm model

The Freundlich isotherm was originally empirical in nature, but has had an intense use to interpret sorption processes on heterogeneous surfaces or on surfaces supporting sites of varied affinities. From this model, the stronger binding sites are first occupied by the sorbate molecules, followed by weaker binding sites in the next step, consequently decreasing the binding strength with the increasing degree of site occupation (Foo and Hameed, 2010). In order to obtain the sorption parameters, Eq. (3) is applied:

$$\log Nf = \log K_F + \frac{1}{n} \log C_s \tag{3}$$

where K_F and n are constants and related to the sorption capacity of the biosorbent and the sorption intensity. The plot of $\log Nf$ versus $\log Cs$ for the sorption was employed to generate K_F and n from the intercept and the slope values, respectively.

2.5.3. Temkin isotherm model

This model was developed by Tempkin and Pyzhev to understand the effects of some indirect sorbate–sorbent interactions on sorption isotherms. It was deduced in these interactions that the heat of sorption of all the molecules in the layer would decrease linearly rather than logarithmic as sorption occurs (Liu and Liu, 2008). The isotherm can be used in the following form:

$$Nf = n_T \ln K_T + n_T \ln C_s \tag{4}$$

A plot of $\ln Cs$ versus Nf enables determination of K_T, n_T and b values. The constant b is related to the heat of sorption, which can be calculated using the following equation:

Table 3 Number of moles sorbed (Nf), the Freundlich (n and K_f), the Temkin (b and K_T) parameters, coefficient of determination (R^2), and the respective error for interaction of divalent metals with activated carbon (prepared at 400 °C for 30, 45 and 60 min) at 25 °C, using linear method.

Time (min)	Isotherm	Constant	Pb(II)	Cu(II)	Ni(II)
30	Freundlich	K_f (mmol g^{-1})	0.62 ± 0.20	0.81 ± 0.08	0.54 ± 0.26
		n	2.60 ± 0.38	3.09 ± 0.32	2.93 ± 0.34
		R^2	0.798	0.847	0.893
		SE	1.32	1.24	1.79
		χ^2	0.97	0.85	1.23
	Temkin	K_T (mmol dm^{-3})	16.07 ± 0.68	45.09 ± 0.88	17.94 ± 0.59
		b (kJ mol^{-1})	612.65 ± 0.24	575.94 ± 0.23	508.01 ± 0.20
		R^2	0.864	0.910	0.944
		SE	0.10	0.09	0.057
		χ^2	0.09	0.075	0.036
45	Freundlich	K_f (mmol g^{-1})	0.49 ± 0.30	0.62 ± 0.20	0.50 ± 0.29
		n	2.72 ± 0.36	2.97 ± 0.36	3.09 ± 0.32
		R^2	0.898	0.780	0.833
		SE	1.45	1.26	2.86
		χ^2	0.76	0.76	1.32
	Temkin	K_T (mmol dm^{-3})	10.39 ± 0.01	15.24 ± 0.64	24.64 ± 0.55
		b (kJ mol^{-1})	0.54 ± 0.02	0.590 ± 0.23	0.42 ± 0.17
		R^2	0.935	0.817	0.910
		SE	0.039	0.082	0.063
		χ^2	0.010	0.062	0.051
60	Freundlich	K_f (mmol g^{-1})	0.96 ± 0.02	0.816 ± 0.02	1.06 ± 0.01
		n	3.32 ± 0.05	3.09 ± 0.04	2.80 ± 0.05
		R^2	0.715	0.847	0.700
		SE	7.13	1.9	2.57
		χ^2	3.27	0.78	1.01
	Temkin	K_T (mmol dm^{-3})	28.34 ± 0.02	45.07 ± 0.02	189.65 ± 0.01
		b (kJ mol^{-1})	0.752 ± 0.02	0.575 ± 0.01	0.221 ± 0.02
		R^2	0.779	0.910	0.757
		SE	0.70	0.68	0.044
		χ^2	0.32	0.59	0.024

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$$n_T = \frac{RT}{b} \quad (5)$$

To evaluate the fitness of the isothermal equation to the experimental equilibrium data, an error function is required to enable the optimization procedure. Three parameters, coefficient of determination (R^2), chi-square χ^2 and the standard error (S.E.) of the estimated values were also used to determine the validity of each model. S.E. can be defined as the square root of the product of SSE, multiplying by a factor related to the division between the unit and the difference between the number of points in each isotherm and the parameters in each model. The mathematical equations that represent the S.E. and chi-square χ^2 are shown in Eqs. (6) and (7):

$$SE = \sqrt{\frac{1}{m-P}\sum_{i=1}^{m}(N_{fexpi} - N_{fcali})^2} \quad (6)$$

$$x^2 = \sum_{i=1}\frac{(N_{fexpi} - N_{fcali})^2}{N_{fcali}} \quad (7)$$

where Nf_{exp} is the number of experimentally sorbed moles, Nf_{calc} is the number of calculated moles from each model, m is the number of points present in each isotherm and P is the number of parameters in each equation (Basha et al., 2008).

3. Result and discussion

The percentage yield of the prepared activated carbons in different heating times prior to washing was different. The activated carbon yields obtained at 400 °C were 54.78%, 52.27% and 50.31% at 30, 45 and 60 min heating times, respectively. The yield of activated carbons decreased as the heating duration increased. As carbonization duration increases from

Table 4 Number of moles sorbed (*Nf*), the Freundlich (n and K_f), Temkin (K_T and b) parameters, coefficient of determination (R^2), and respective error for interaction of Cu^{2+}, Pb^{2+} and Ni^{2+} with activated carbon (prepared at 400 °C for 30, 45, and 60 min) at 25 °C, using non-linear method.

Time (min)	Isotherm	Constant	Cu(II)	Pb(II)	Ni(II)
30	Langmuir	Nf (mmol g^{-1})	1.17	1.01	0.93
		N_s (mmol g^{-1})	1.28 ± 0.03	1.20 ± 0.05	1.05 ± 0.02
		b (g mmol^{-1})	2.94 ± 0.32	1.47 ± 0.24	1.43 ± 0.10
		R^2	0.979	0.942	0.988
		χ^2	0.002	0.004	0.003
	Freundlich	K_f (mmol g^{-1})	0.84 ± 0.04	0.67 ± 0.04	0.57 ± 0.03
		n	3.98 ± 0.71	3.39 ± 0.63	3.53 ± 0.48
		R^2	0.847	0.800	0.887
		χ^2	0.019	0.016	0.007
	Temkin	K_T (mmol dm^{-3})	45.09 ± 19.62	15.43 ± 5.94	18.01 ± 4.97
		b (kJ mol^{-1})	4.30 ± 0.47	3.98 ± 0.48	4.88 ± 0.39
		R^2	0.921	0.884	0.949
		χ^2	0.009	0.009	0.005
45	Langmuir	Nf (mmol g^{-1})	0.93	0.80	0.83
		N_s (mmol g^{-1})	1.15 ± 0.07	0.99 ± 0.03	0.93 ± 0.02
		b (g mmol^{-1})	1.32 ± 0.27	1.05 ± 0.11	1.61 ± 0.15
		R^2	0.901	0.973	0.981
		χ^2	0.004	0.001	0.0009
	Freundlich	K_f (mmol g^{-1})	0.65 ± 0.04	0.51 ± 0.02	0.54 ± 0.03
		n	3.52 ± 0.74	3.08 ± 0.41	4.10 ± 0.72
		R^2	0.780	0.896	0.837
		χ^2	0.009	0.003	0.008
	Temkin	K_T (mmol dm^{-3})	15.24 ± 8.23	10.39 ± 2.81	25.28 ± 10.87
		b (kJ mol^{-1})	4.19 ± 0.69	4.59 ± 0.42	5.85 ± 0.62
		R^2	0.840	0.943	0.916
		χ^2	0.006	0.003	0.004
60	Langmuir	Nf (mmol g^{-1})	0.83	0.63	0.55
		N_s (mmol g^{-1})	0.91 ± 0.02	0.74 ± 0.03	0.61 ± 0.04
		b (g mmol^{-1})	2.94 ± 0.32	1.83 ± 0.36	3.97 ± 0.01
		R^2	0.979	0.890	0.906
		χ^2	0.001	0.002	0.001
	Freundlich	K_f (mmol g^{-1})	0.60 ± 0.03	0.45 ± 0.02	0.46 ± 0.02
		n	3.98 ± 0.73	4.13 ± 0.88	5.68 ± 1.50
		R^2	0.847	0.736	0.755
		χ^2	0.009	0.006	0.002
	Temkin	K_T (mmol dm^{-3})	45.09 ± 19.62	28.34 ± 18.20	189.65 ± 23.75
		b (kJ mol^{-1})	6.02 ± 0.66	7.25 ± 1.21	11.17 ± 2.52
		R^2	0.921	0.801	0.798
		χ^2	0.005	0.004	0.002

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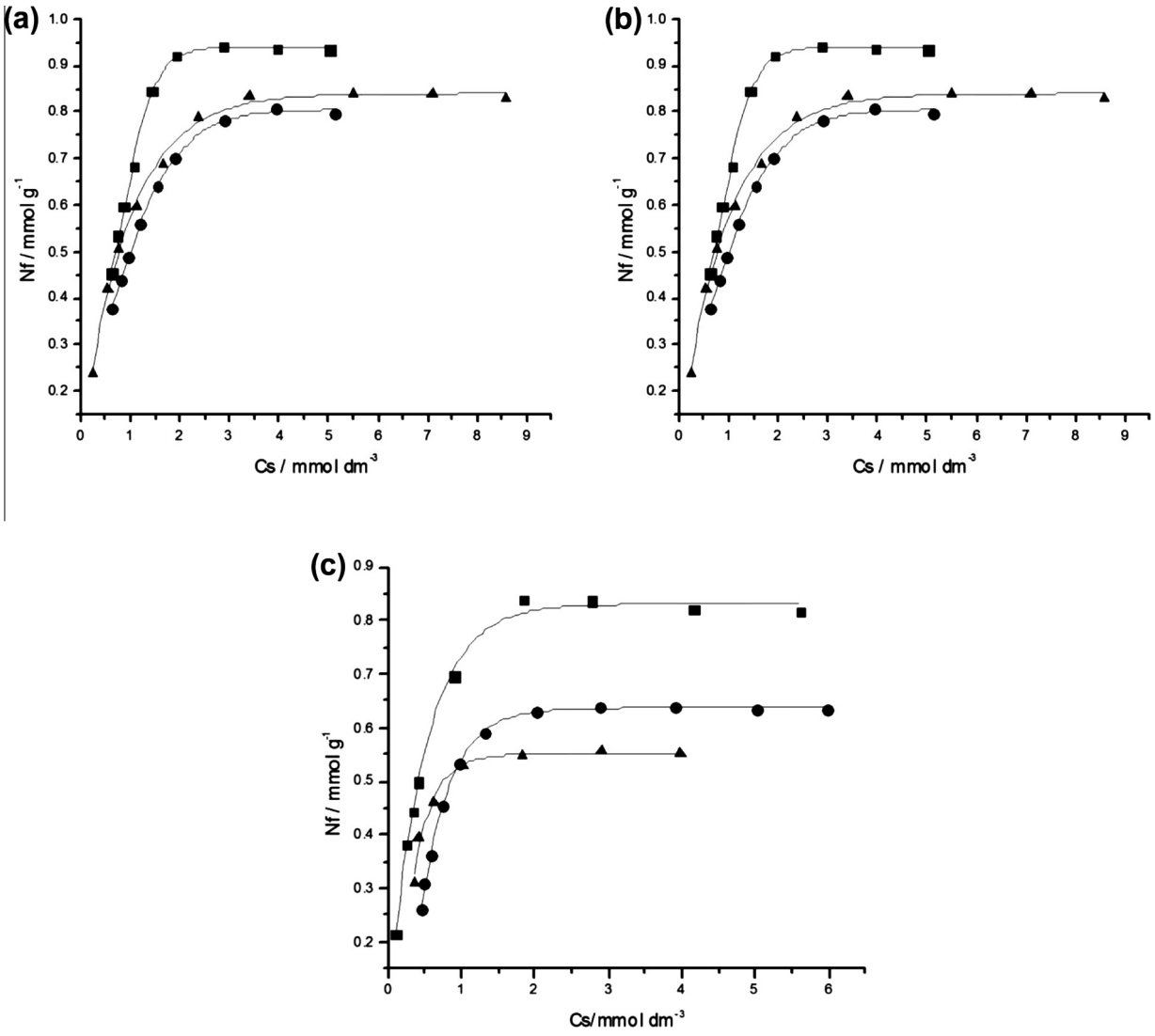

Figure 1 Experimental sorption isotherm of activated carbon prepared at 400 °C for (a) 30 (b) 45, and (c) 60 min. The line with points (●), (■), and (▲) represents lead, copper, and nickel, respectively.

30 min to 60 min at 400 °C, the surface area decreased from 375 to 27 m^2/g. Due to increase in heating duration, some of the pores become larger or even collapse, thus contributing to the reduction of surface area (Table 1), (Diao et al., 2001).

The use of phosphoric acid during activation promotes depolymerization, dehydration, and redistribution of constituent biopolymers and also favoring the conversion of aliphatic to aromatic compounds (Prahas et al., 2008; Rodriguez-Reinoso and Molina-Sabio, 1992).

3.1. Sorption study

Activated carbon, thus prepared was applied to study the sorption process of divalent cations of lead, copper and nickel from aqueous solutions. The quantity of cations sorbed *Nf,* the maximum sorption capacity *N*s, the interaction energy *b* and the coefficient of determination (R^2) were obtained from the linearized form of the Langmuir model (Table 2).

Experimental and linear form of the Langmuir sorption isotherm for nickel on activated carbon was prepared at 30 min heating time (Fig. 1). Activated carbon prepared at different heating times showed different sorption capacity. Activated Carbon prepared at 30 min heating time showed a greater sorption capacity for Cu^{2+}, Pb^{2+} and Ni^{2+} and its order of cation sorption is $Cu^{2+} > Pb^{2+} > Ni^{2+}$. An increase in time for the preparation of activated carbon gives a smaller surface area and hence, causes decrease in the sorption capacity of cations.

The Langmuir, the Freundlich and the Temkin models are the three most common isothermal models that are used to describe these systems in equilibrium at solid/liquid interface. The Langmuir isotherm can be transformed to at least four linear forms and all of them were applied to this sorption study. The parameters of these equations and equilibrium models often lead us to understand the mechanisms of sorption, surface properties and affinity of the sorbent. Both linear and

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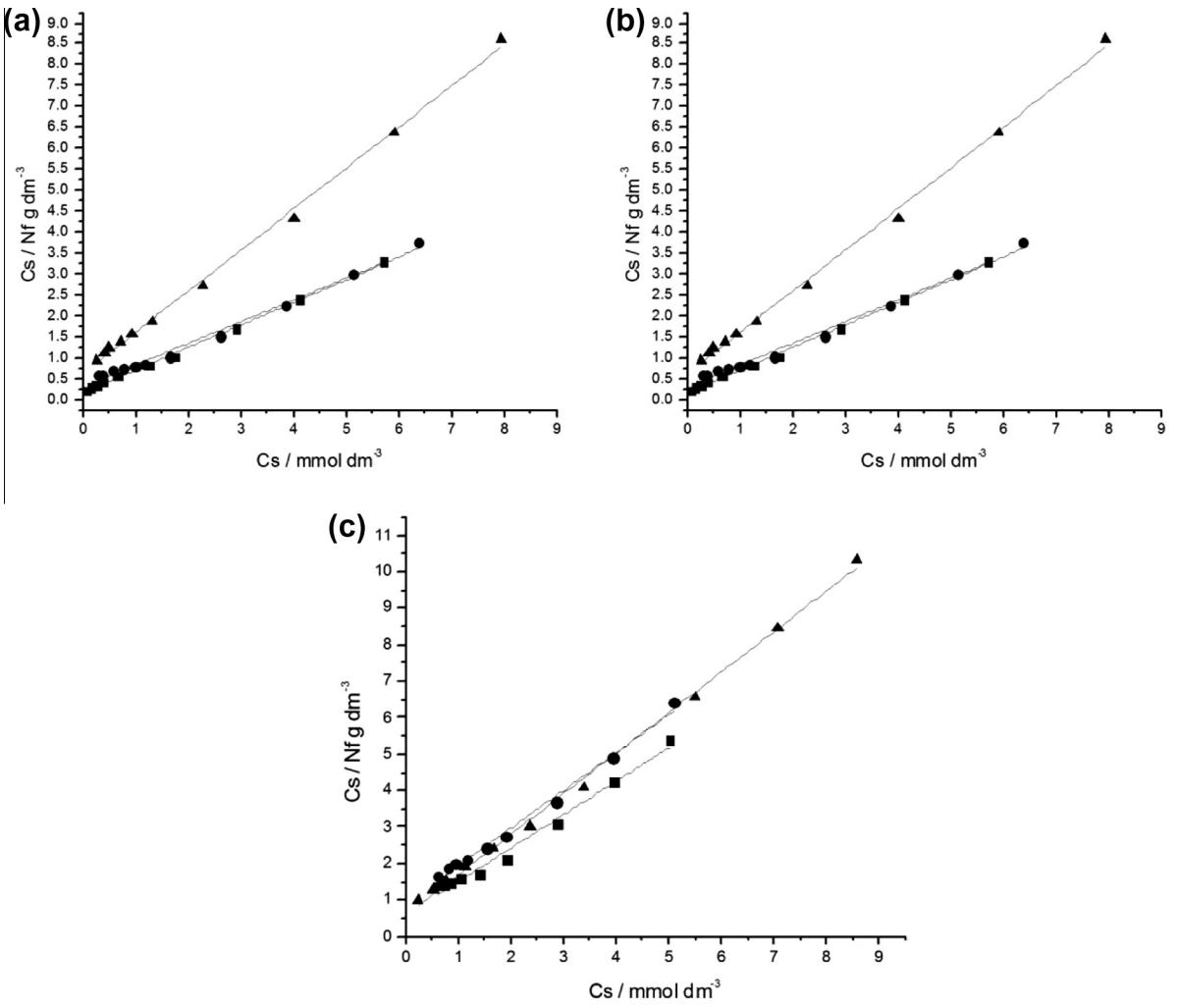

Figure 2 Linear form of the Langmuir sorption isotherm for copper (■), lead (●) and nickel (▲) of activated carbon at (a) 30 °C, (b) 45 °C, and (c) 60 °C.

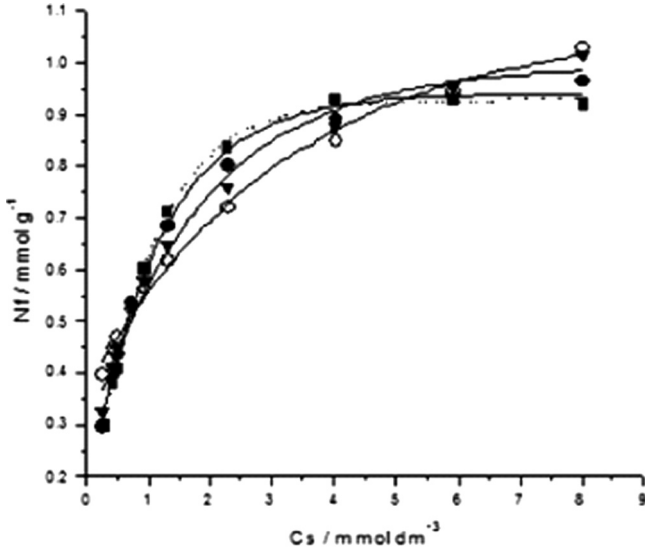

Figure 3 Experimental and nonlinear (■) Langmuir (●), Freundlich (○) and Temkin (▼) sorption isotherm for copper prepared at 30 °C.

non-linear regression analysis were used to evaluate sorption process to ensure better results. It was observed that the predicted values of constant and the correlation coefficients values for all four linear forms of the Langmuir isotherms are quite different (Table 2). The value of coefficient of determination obtained from the Langmuir isotherm, type 1, is greater than for the other three linear equations. It suggests that the Langmuir type 1 fits better to the experimental data in comparison with the other linear forms of the Langmuir isotherm. Error functions, SE, and chi-square χ^2 showed minimum values for the Langmuir model type 1, than other three types of the Langmuir equations that suggest that the Langmuir model type 1 fits better experimental data for sorption on activated carbons prepared at different heating times. The excellent fitness of the Langmuir isotherm type 1 to the experimental data confirms that the sorption occurs in monolayer, each molecule has the same activation energy and the interaction sorbate/sorbate is negligible. The error functions for the Freundlich isotherms showed higher values than the Langmuir isotherm of type 1, (Table 2) for all the material, but gave lower values for the Temkin model (Table 3), as compared to the other three forms of the linear Langmuir isotherms.

When the error value functions of the other three linear forms of the Langmuir isotherm are compared with those of the Freundlich, it is less appropriate to describe the sorption system than the other three models of the Langmuir (Fig. 2). The isothermal parameters of the three models were also determined by using the non-linear regression analysis. It is to be noted that the values of constants of the Langmuir isotherm, determined by this method, are very close to the results of the Langmuir model Type 1. However, the values of different error functions corresponding to the non-linear Langmuir equation are smaller than those of the Freundlich and the Temkin models (Table 4 and Fig. 3). The non-linear regression analysis corresponds to the best way to select the isotherm that fits the experimental data. This method involves an attempt to minimize the distribution of errors between experimental data and the isotherm considered (Sousa et al., 2009). Both linear and non-linear regression analysis produce different models as the best fitting isotherm for the given set of data, thus indicating a significant difference between the analytical methods.

4. Conclusion

S. persica was used for the preparation of activated carbon under vacuum. The study showed that with the increase in heating time, the surface area of the activated carbon decreased. The decrease in surface area may be attributed to the increase in pore diameter to an extent that it collapsed and thus caused a decrease in surface area.

Activated carbon was applied for copper, lead and nickel sorption from dilute aqueous solutions. The maximum sorption capacities were found for copper, obtained through the Langmuir sorption isotherm. The activated carbon prepared at 30 min heating time, showed maximum sorption capacities for cations due to its large surface area.

The experimental data were adjusted to the Langmuir, the Freundlich and the Temkin sorption isotherms using both linear and non linear regression methods. Four types of Langmuir linear equations were used for a better comparison of linear and non linear regression methods. The Langmuir model type 1 provided the lowest error values and fits better to experimental data compared with the latter two models.

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References

Ajmal, M., Khan, A.H., Ahmad, S., Ahmad, A., 1998. Water Res. 32, 3085–3091.
Allen, S.J., Mckay, G., Porter, J.F., 2004. J. Colloid Interface Sci. 280, 322–333.
Badshah, S., Airoldi, C., 2011. Chem. Eng. J. 166, 420–427.
Baker, H., Khalili, F., 2004. Anal. Chim. Acta 516, 179–186.
Basha, S., Murthy, Z.V.P., Jha, B., 2008. Ind. Eng. Chem. Res. 47, 980–986.
Diao, Y., Walawender, W.P., Fan, L.T., 2001. Bioresour. Technol. 81, 45–52.
Faust, S.D., Ali, O.M., 1983. Chemistry of Water Treatment. Butterworth, Boston, p. 114.
Foo, K.Y., Hameed, B.H., 2010. Chem. Eng. J. 156, 2–10.
Hassler, J.W., 1993. Activated Carbon. Chemical Publishing Company, Inc., N.Y.
Hassler, J.W., 1974. Purification with Activated Carbon. Chemical Publishing Co. NY. p. 169.
Huang, C.P., Hao, O.J., 1989. Environ. Technol. Lett. 10, 863–874.
Khan, A., Badshah, S., Airoldi, C., 2011. Chem. Eng. J. 171, 159–166.
Liu, Y., Liu, Y.J., 2008. Sep. Purif. Technol. 61, 229–242.
Lo, W., Chua, H., Lam, K.H., Bi, S.P., 1999. Chemosphere 39, 2723–2736.
Lothenbach, B., Furrer, G., Schulin, R., 1997. Environ. Sci. Technol. 31, 1452–1462.
Mattson J.S., Mark, H.H., 1971. Activated Carbon. Marcel Dekker, Inc., N.Y.
Meunier, N., Drogui, P., Montane, C., Hausler, R., Mercier, G., Blais, J.F., 2006. J. Hazard. Mater. 137, 581–590.
Molina-Sabio, M., Rodrigues-Reinoso, F., 2004. Colloids Surf. A 241, 15–25.
Ng, J.C.Y., Cheung, W.H., McKay, G., 2002. J. Colloid Interface Sci. 255, 64–74.
Ngah, W.S., Fatinathan, S., 2008. Chem. Eng. J. 143, 62–72.
Oh, S., Kwak, M.Y., Shin, W.S., 2009. Chem. Eng. J. 152, 376–388.
Oliver, M.A., 1997. Eur. J. Soil Sci. 48, 573–592.
Prahas, D., Kartika, Y., Indraswati, N., Ismadji, S., 2008. Chem. Eng. J. 140, 32–42.
Qin, Y., Cai, L., Feng, D., Shi, B., Liu, J., Zhang, W., Shen, Y., 2007. J. Appl. Polym. Sci. 104, 3581–3587.
Rodriguez-Reinoso, F., Molina-Sabio, M., 1992. Carbon, 30, 11–18.
Sikalidis, C.A., Alexiades, C., Misaelides, P., 1989. Toxicol. Environ. Chem. 20/21, 175–180.
Sousa, K.S., Silva-Filho, E.C., Airoldi, C., 2009. Carbohydr. Res. 344, 1716–1723.
Volesky, B., 1990. Biosorption of Heavy Metals. CRC Press, Boca Raton.
Xie, J.Z., Chang, H.L., Kilbane, J.J., 1996. Bioresour. Technol. 57, 127–136.
Zamzow, M.J., Eichbaum, B.R., Sandgren, K.R., Shanks, D., 1990. E. Sep. Sci. Technol. 25, 1555–1569.
Zdemir, C.O., Karatas, M., Dursun, S., Argun, M.E., Dogan, S., 2005. Environ. Technol. 26, 397–400.

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